Analysis of Perchlorate in Groundwater by Electrospray Ionization Mass Spectrometry/Mass Spectrometry

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An electrospray ionization mass spectrometry/mass spectrometry (ESI/MS/MS) method was developed to measure *part-per-billion (μg/L)* concentrations of perchlorate in groundwater. Selective and sensitive perchlorate detection was achieved by operating the mass spectrometer in the negative ionization mode and by using MS/MS to monitor the ClO_4^- to ClO_3^- transition. The method of standard additions was used to address the considerable signal suppression caused by anions that are typically present in groundwater, such as bicarbonate and sulfate. ESI/MS/MS analysis was rapid, accurate, reproducible, and provided a detection limit of 0.5 μg/L perchlorate in groundwater. Accuracy and precision of the ESI/MS/MS method were assessed by analyzing performance evaluation samples in a groundwater matrix (4.5−75 μg/L perchlorate) and by comparing ion chromatography (IC) and ESI/MS/MS results for local groundwater samples (<0.5−35 μg/L perchlorate). Results for the performance evaluation samples differed from the certified values by 4−13%, and precision ranged from 3 to 10% (relative standard deviation). The IC and ESI/MS/MS results were statistically indistinguishable ($P > 0.05$) for perchlorate concentrations above the detection limits of both methods.

Introduction

Since the California Department of Health Services (DHS) developed a sensitive ion chromatography (IC) method for the determination of perchlorate in water in 1997, perchlorate has been detected in approximately 145 public water sources in California and has also been detected in drinking water sources in Nevada and Utah (*1, 2*). Ingestion of perchlorate constitutes a health concern because the anion can reduce thyroid hormone production by competitively inhibiting iodide uptake (*1, 2*). To protect human health, DHS issued an action level of 18 μg/L perchlorate in California drinking water supplies (*1*). To date, detections of perchlorate in groundwater have reflected major industrial uses of ammonium perchlorate, namely, as a component of solid propellants for rockets, missiles, and fireworks. Systematic national studies of perchlorate contamination in drinking water sources have not yet been conducted. Accurate, sensitive, reliable, and rapid analyses for perchlorate in aqueous media are needed to characterize, and ultimately minimize, the risk of perchlorate exposure (*2*).

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Ion chromatography (IC) with electrochemical conductivity detection is commonly used to determine perchlorate in aqueous matrices. Typical IC detection limits for perchlorate in drinking water are 0.3−0.7 μg/L, and typical reporting limits are 2.5−4 μg/L (*3, 4*). Mass spectrometric techniques, such as inductively coupled plasma mass spectrometry, have also been used to determine inorganic compounds that are structurally similar to perchlorate. Bromide and bromate have been measured by negative thermal ionization mass spectrometry and by inductively coupled plasma mass spectrometry at detection limits of 0.03−0.09 μg/L (*5*). Oxyhalides, such as chlorate, have been measured by IC coupled with ionspray tandem mass spectrometry at detection limits of 0.05−1 μg/L (*6, 7*). Tsui is reportedly working on an ESI/MS method for determining 1 μg/L concentrations of perchlorate (*8*); however, little information regarding this method was found during a survey of peer-reviewed literature. This article describes a mass spectrometric technique (ESI/MS/MS) with a nontoxic eluent (water) that offers performance superior to IC in terms of detection limits and compound confirmation.

Experimental Section

Reagents and Standards. Reagent water (18 MΩ resistance) was obtained from a Milli-Q UV Plus system (Millipore, Bedford, MA). Sodium perchlorate, 99% purity, was purchased from Aldrich (Milwaukee, WI). New perchlorate standards were made monthly and stored at 4 °C. Perchlorate standards and spiking solutions were prepared from a stock solution that contained 1 mg/mL (10 mM) ClO_4^- in reagent water. Performance evaluation standards for perchlorate were purchased from Environmental Resource Associates (Arvada, CO). Ultrahigh purity (99.999%) nitrogen was used as a nebulizer and desolvation gas and ultrahigh purity (99.999%) argon was used as a collision gas for ESI/MS/MS.

Sample Collection. Samples were collected in precleaned, 40-mL VOA vials. All vials were completely filled with groundwater, leaving no headspace. Samples were stored at 4 °C prior to analysis and were analyzed within 1 month, in accordance with recommendations for storage and handling provided by other analytical methods (*3, 4*). It has been reported that perchlorate in laboratory water is stable for up to 109 days under conditions of controlled room temperature and light intensity (*8*).

Sample Preparation. All samples were filtered through a 0.45 μm UNIPREP membrane filter, with a Nylon-66 membrane (Whatman, Clifton, NJ). Tests demonstrated that this filter did not alter perchlorate concentrations detectably in aqueous samples.

Because the method of standard additions (*9*) was used for perchlorate quantification, a series of spiked samples was prepared. Thus, 1.00-mL aliquots of sample were measured into four 2-mL autosampler vials (Waters, Milford, MA). No perchlorate was added to the first vial. Three additional vials containing the sample were spiked such that the concentration of added perchlorate was either 10, 20, or 40 μg/L.

ESI/MS/MS Conditions. The Quattro LC mass spectrometer (Micromass, Inc., Manchester, UK), equipped with a Waters 2690 Separations Module and a Waters 996 Photodiode Array Detector (Waters, Milford, MA), was operated in the electrospray, negative ionization mode. No LC column was required for perchlorate analysis; however, the system was operated with a guard column (Nova-Pak C18, 60 Å, 4-μm particle size, 3.9-mm i.d. by 20-mm length, Waters, Milford, MA) to protect the MS from hydrophobic organic compounds. A 20-μL sample was injected into the system
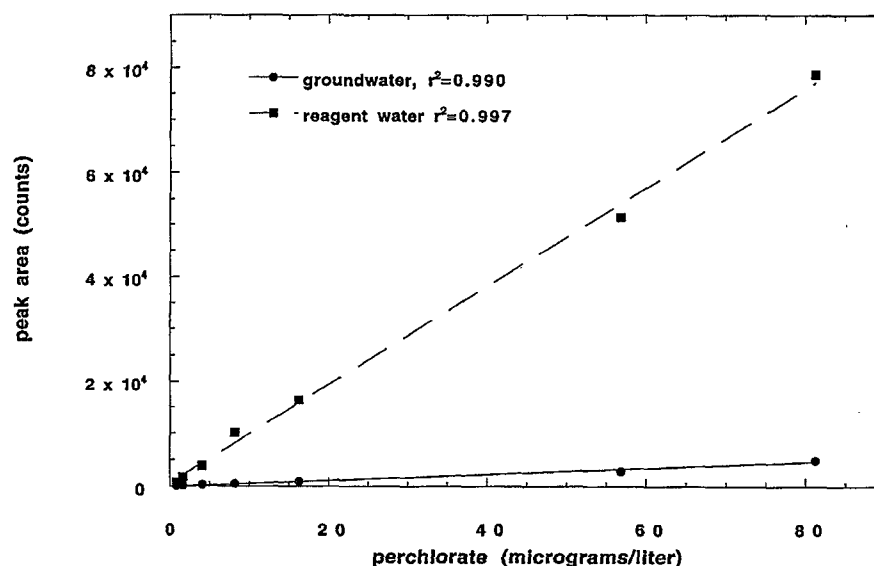
FIGURE 1. Calibration curves for perchlorate in reagent (18 MΩ) water and in groundwater.

using an LC mobile phase of 100% water at a flow rate of 250 μL/min. The retention time for perchlorate was < 2 min; thus analysis of a sample set (i.e., the unspiked sample and the three associated spiked samples) required < 8 min, which is comparable to the analysis time for one sample by IC (3).

Selected reaction monitoring (also known as multiple reaction monitoring) was used to monitor the transition from m/z 99 to m/z 83 for perchlorate quantification. The transition from m/z 101 (^{37}Cl isotope peak) to m/z 85 was monitored to confirm perchlorate's identity. Each reaction was monitored for a 0.5-s dwell time at a cone voltage of 45 V and collision energy of 23 eV. The collision cell was pressurized to ca. 1.2×10^{-4} kPa with argon. Other operating conditions of the ESI/MS/MS were as follows: 2.5 kV capillary voltage, 3 V extraction cone voltage, 80 °C source block temperature, 400 °C desolvation temperature, 80 L/h nebulizer gas flow, and 350 L/h desolvation gas flow. To ensure optimal detection limits and reproducibility, the sample cone of the ESI/MS/MS was cleaned daily according to the manufacturer's instructions.

Sample Analysis and Quantification. Blanks and performance evaluation samples were analyzed daily with each set of samples. Each sample set (i.e., the unspiked sample and the three associated spiked samples) was analyzed in series.

The mass spectral peaks produced by the transitions from m/z 99 to m/z 83 and from m/z 101 to m/z 85 were integrated, and their ratios were examined in unspiked samples to check for interferences. Values that differed from the natural isotopic ratio of 3.08 by more than 5% were suspect and prompted reanalysis.

A plot of integrated peak area versus added perchlorate concentration was generated for each sample set. A linear regression equation was determined for each plot and was used to calculate the perchlorate concentration of the unspiked sample. If r^2 values were less than 0.990, the native samples were respiked and reanalyzed. Sample sets with native perchlorate concentrations exceeding ca. 40 μg/L required dilution before reanalysis.

Results and Discussion

Method detection limits were determined by analyzing eight replicate injections of a perchlorate solution and by considering the standard deviation of their measurement (10). A solution of 0.47 μg/L perchlorate was used to determine

the method detection limit in reagent water, and a solution of 4.8 μg/L perchlorate was used to determine the method detection limit in perchlorate-free groundwater. Method detection limits for perchlorate in reagent water and in perchlorate-free groundwater were 0.1 and 0.5 μg/L, respectively. The groundwater used to determine the 0.5 μg/L detection limit had relatively high concentrations of the three major anions that occur in groundwater: bicarbonate (1.8 mM), chloride (2.5 mM), and sulfate (2.3 mM). The concentrations of the latter two anions were in the range of the 90th percentile concentrations found in U.S. terrestrial waters (11). A detection limit of 0.5 μg/L also applied to artificial groundwater that consisted of reagent water amended with all three major anions at their 90th percentile concentrations (including 6.7 mM bicarbonate).

Calibration curves for perchlorate were linear between 0.8 and 80 μg/L, in both reagent water and in groundwater (Figure 1). When perchlorate was analyzed in groundwater, severe signal suppression (e.g., >90% suppression relative to the response in reagent water) was caused by anions (e.g., bicarbonate, chloride, and sulfate) that were present in solution at much higher concentrations than perchlorate (Figure 1). Signal suppression caused by nontarget ions in solution is a well-documented problem for ESI/MS (12, 13). Data for both calibration plots in Figure 1 were collected on the same day under the same instrument conditions; thus, the differences in the calibration curves were matrix-related. The severe signal suppression observed when analyzing perchlorate in groundwater necessitated use of the method of standard additions for accurate quantification.

Several performance evaluation samples were analyzed by ESI/MS/MS. Performance evaluation stock solutions were obtained from an outside laboratory and were diluted 10-fold with perchlorate-free groundwater. The results of ESI/MS/MS analysis are shown in Figure 2. Measured concentrations of perchlorate in the standards certified to contain 4.5, 37.5, and 75 μg/L were 3.9, 36.2, and 79.2 μg/L of perchlorate, respectively. Agreement between measured and certified values for the mid- and high-concentration samples was within approximately 6%; the measured perchlorate concentration for the low concentration standard was 13% below the certified value. The precision of the performance evaluation measurements was also favorable; the relative standard deviations observed for triplicate measurements of perchlorate ranged from 3 to 10%.
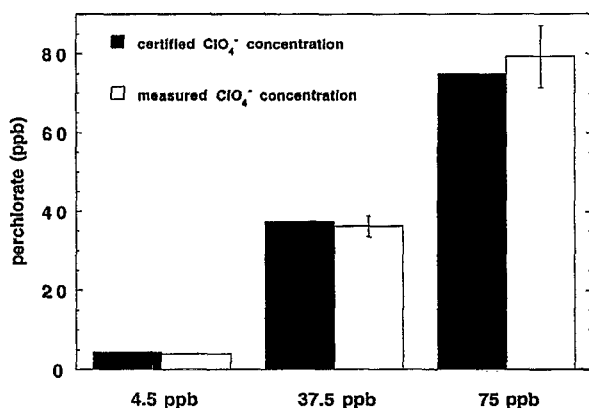
FIGURE 2. Perchlorate concentrations in performance evaluation samples measured by ESI/MS/MS. All samples were diluted in perchlorate-free groundwater. Each measured value represents the average of three analyses; error bars represent one standard deviation.

TABLE 1. Comparison of Perchlorate Concentrations in Groundwater Samples Measured by ESI/MS/MS and by Ion Chromatography (IC)

sample ID	perchlorate concn (μg/L) ESI/MS/MS	IC	sample ID	perchlorate concn (μg/L) ESI/MS/MS	IC
A	ND[a]	ND	N	17	13
B	ND	ND	O	15	14
C	ND	ND	P	16	14
D	ND	ND	Q	14	16
E	ND	ND	R	21	18
F	ND	ND	S	20	19
G	ND	ND	T	19	22
H	ND	ND	U	33	23
I	ND	ND	V	27	25
J	0.6	ND	W	32	32
K	0.7	ND	X	29	35
L	1	ND	Y	37	35
M	16	12			

[a] ND indicates that no perchlorate was detected in the sample at detection limits of 0.5 μg/L (ESI/MS/MS) or 4 μg/L (IC).

The ESI/MS/MS method was used to determine perchlorate concentrations in local groundwater samples. The collected samples were split so that each sample could also be analyzed by the state-certified IC method (3) at an independent laboratory. The results of these analyses are shown in Table 1. For the 13 samples in which perchlorate was detected by both methods, the difference between perchlorate concentrations measured by ESI/MS/MS and by IC averaged 15%. No systematic biases were observed, and the results for the two methods were statistically indistinguishable (t-test, $P > 0.05$, $n = 13$). Furthermore, semiquantitative agreement between the two methods was observed for samples in which perchlorate was not detected by IC; in samples J−L (Table 1), perchlorate was detected by ESI/MS/MS at concentrations below the IC reporting limit. The two methods also concurred that perchlorate was not detectable in samples A−I.

ESI/MS/MS is a rapid, sensitive, specific, and accurate technique for the determination of perchlorate in groundwater that offers several advantages over existing methods.

The high degree of specificity of ESI/MS/MS precludes the potential interference problems in IC caused by coeluting compounds. Such specificity could be crucial for resolving contested analytical results, such as reports of perchlorate concentrations in fertilizers of 0.15−0.84 wt % (14). In addition, some methods for perchlorate analysis require 4-cyanophenol (3), which is toxic and can produce hydrogen cyanide under acidic conditions. ESI/MS/MS does not require the use of this toxic reagent or toxic organic eluents, such as acetonitrile. Finally, the results of the comparison between ESI/MS/MS and IC with 25 groundwater samples suggest that the ESI/MS/MS method performs at least as well as the California-certified IC method when used to analyze groundwater with perchlorate concentrations in the range of the 18 μg/L DHS action level. The relatively high sensitivity of the ESI/MS/MS method (i.e., detection limits that are <5% of the action level) and its accuracy at low concentrations (Figure 2) allow the method to be particularly useful for delineating plume boundaries, which are needed for regulatory purposes as well as an improved understanding of the transport and fate of perchlorate in groundwater.

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